ORIGINAL ARTICLE

The status of phosphorus in Thai soils and P evaluation using EDTA-NaF extraction method

Phairat Phimsirikul[1] **and Toru Matoh**[2]

Abstract

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Although the available P extracted by Bray II method in tropical soil is low, most of tropical plants can grow well. The objective of this study was to study P status and to evaluate the available P extracted by EDTA-NaF method. Top soil and sub soil of 10 dominant soil series in Thailand were analyzed for some chemical properties and characterization of the forms of phosphorus using EDTA-NaF extraction and successive phosphorus extraction by the modified Sekiya method. The soil total P concentration was 38-1137 mg P_2O_5 kg^{-1}. The available Bray II-P was very low to high (1-76 mg P_2O_5 kg^{-1}), and it approximated 0.17-12% of the total P. Iron and aluminum phosphates were the main fraction of inorganic P in acid soil, whereas Ca phosphates were in calcareous soils. Organic P content accounted for 33-67% and most of them were bound with Fe and Al in acid soils and Ca in calcareous soils. P extracted by EDTA-NaF reagent was obviously larger than that of Bray II reagent. The EDTA-NaF extracted P [high molecular weight organic P (HMWP)+ inorganic P (EDTA ext P_i)] was 7-46% and 1-6% of total P in acid soils and calcareous soils respectively. The EDTA ext P_i tended to be larger than HMWP except in Tk soil. The total amount of extracted P correlated well with Al-P_i and Fe-P_i which were the main fraction of inorganic P. It also correlated with HMWP, but

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[1] **M.Sc.(Soil Science), Department of Soil Science, Faculty of Agricultural Technology, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand** [2] **Ph.D.(Plant Nutrition), Assoc. Prof., Laboratory of Plant Nutrition, Division of Applied Life Sciences, Graduate School of Agriculture, Kyoto University, Kyoto 606-8502, JAPAN**
Corresponding e-mail: kpphaira@kmitl.ac.th
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HMWP did not correlate with organic P determine by ignition method and Ca-P_o, Fe-P_o and Al-P_o. The EDTA-NaF method may be suitable for P evaluation in the soils which have high amounts of Fe-P_i, Al-P_i and organic P widely distributed in Thailand.

Key words : Ethylenediamine tetraacetic acid (EDTA), high molecular weigh organic phosphate (HMWP), Thai soil, fractionation P.

บทคัดย่อ

ไพรัตน์ พิมพ์ศิริกุล[1] และ Toru Matoh[2]

สถานะของฟอสฟอรัสในดินของไทยและการประเมินระดับฟอสฟอรัสโดยวิธีสกัดด้วย EDTA-NaF

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ถึงแม้ว่าฟอสฟอรัสที่เป็นประโยชน์ที่สกัดโดยวิธี Bray II ในดินเขตร้อนมีค่าต่ำ แต่พืชในเขตร้อนโดยทั่วไปมักเจริญเติบโตได้ดี วัตถุประสงค์ของการทดลองในครั้งนี้เพื่อศึกษาสถานะฟอสฟอรัสและประเมินฟอสฟอรัสที่เป็นประโยชน์ในดิน โดยเก็บตัวอย่างดินที่พบโดยทั่วไปในประเทศไทย 10 ชุดดิน นำมาวิเคราะห์สมบัติทางเคมีและสกัดฟอสฟอรัสโดยใช้ EDTA-NaF สกัดหาฟอสฟอรัสรูปต่าง ๆ โดยดัดแปลงวิธีของ Sekiya จากการทดลองพบว่าฟอสฟอรัสทั้งหมดในดินมีค่า 38-1,137 mg P_2O_5 kg^{-1} ฟอสฟอรัสที่สกัดโดยวิธี Bray II มีค่าต่ำมากจนถึงสูง (1-76 mg P_2O_5 kg^{-1}) หรือประมาณ 0.17-12% ของฟอสฟอรัสทั้งหมด ในดินกรดพบว่าอนินทรีย์ฟอสฟอรัสส่วนใหญ่อยู่ในรูปเหล็กและอะลูมินัมฟอสเฟต ในขณะที่ในดินเนื้อปูนส่วนใหญ่เป็นแคลเซียมฟอสเฟต อินทรีย์ฟอสฟอรัสมีประมาณ 33-66% ของฟอสฟอรัสทั้งหมด โดยส่วนใหญ่จับอยู่กับเหล็กและอะลูมินัม และแคลเซียม ในดินกรด และดินเนื้อปูน ตามลำดับ ฟอสฟอรัสที่สกัดด้วย EDTA-NaF มีค่าสูงกว่าที่สกัดด้วย Bray II อย่างชัดเจน โดยสามารถสกัดอินทรีย์ฟอสฟอรัสที่มีน้ำหนักโมเลกุลสูง (HMWP) และอนินทรีย์ฟอสฟอรัสซึ่งสกัดได้เพียง 7-46% และ 1-6% ของฟอสฟอรัสทั้งหมดในดินกรดและดินเนื้อปูน ตามลำดับ โดยที่อนินทรีย์ฟอสฟอรัสที่สกัดได้มีแนวโน้มสูงกว่า HMWP ยกเว้นในดินตาคลี ปริมาณที่สกัดได้มีความสัมพันธ์กับอนินทรีย์ฟอสเฟตของเหล็กและอะลูมินัมซึ่งเป็นส่วนที่พบมาก นอกจากนั้นยังสัมพันธ์กับ HMWP แต่ไม่พบความสัมพันธ์ระหว่าง HMWP กับอินทรีย์ฟอสฟอรัสที่จับอยู่กับแคลเซียม เหล็ก อะลูมินัม และอินทรีย์ฟอสฟอรัสที่วิเคราะห์โดยวิธีเผา วิธีการสกัดโดยใช้ EDTA-NaF นี้อาจจะเหมาะสมในการใช้ประเมินฟอสฟอรัสในดินที่มีอินทรียฟอสฟอรัส และอนินทรียฟอสฟอรัสอยู่ในรูปของเหล็กและอะลูมินัมซึ่งพบโดยทั่วไปในประเทศไทย

Phosphorus (P) is an important nutrient element which limits agricultural production in the tropics because it is extremely chemically reactive and always exists as insoluble phosphate mineral in nature. Therefore, the available P in tropical soils is low. Soil P can be classified as organic and inorganic P. Most inorganic phosphorus compounds in soils fall into one of two groups: (i) those containing calcium, and (ii) those containing iron and aluminum (Brady and Weil, 1996). Relatively little is known about the chemistry of organic P in soils. Principal forms are the inositol phosphates (10-50%), nucleic acids or their degradation products (1-5%), and phospholipids (0.2-2.5%) (Stevenson, 1986). It is important to emphasize that 20-80% of P is found in the orga-

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[1] ภาควิชาปฐพีวิทยา คณะเทคโนโลยีการเกษตร สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง กรุงเทพฯ 10520 [2] Laboratory of Plant Nutrition, Division of Applied Life Sciences, Graduate School of Agriculture, Kyoto University, Kyoto 606-8502, JAPAN

nic form, especially in the highly weathered soils, this fraction is generally as high as 80% (Foth and Ellis, 1997). The remainder is found in the inorganic fraction containing at least 170 different minerals (Holford, 1997). In tropical soils which are acidic and contain a large amount of Fe and Al, available P is readily precipitated as the highly insoluble iron and aluminum phosphates or adsorbed to oxide surface. Both forms are poor sources of P for higher plants (Stevenson, 1986). In calcareous soils which contain a large amount of Ca, most of the inorganic P precipitates as calcium phosphates. The study of inorganic and organic P of 32 upland soils and 39 paddy soils in Thailand revealed that soil P comprised 65% inorganic P and 35% organic P (Saengthong, 1991), whereas paddy soils P comprised 77% and 23% (Saengthong and Cholitkul, 1989), respectively. However, most of the P in some highly weathered soils in peninsular Thailand consists of organic P (48-71% of the total P), and iron and aluminum phosphates were major forms of inorganic P (Onthong *et al*, 1999). Both inorganic and organic forms of P are important to plants as sources of this element. In general, most of the P, especially in tropical soils, is in forms that are not available for plants because they form complexes with Fe and Al. However, some plants such as *Pueraria phaseoloides, Brachiaria ruziziensis* and *Stylosanthes hamata*, as well as *Anacardium occidentale* L. and *Acacia mangium*, grow well even where the available P in soil, as measured by the Bray II-P method, which is widely used in Thailand, is low. This phenomenon is possibly explained by the amount of P extracted by this method being re-adsorbed during filtration (Takahashi, 1999) or by the ability of plant roots to secrete organic acids which are generally important for mobilizing soil phosphorus (Marshner,1995). These organic acids function as chelating agents by forming complexes with iron and aluminum, and then enable the release of P into the soil solution. Also the synthetic chelating agents, such as EDTA, function as do organic acids. Extractants containing EDTA such as EDTA-NaF are widely used in most Japanese soils high in Al. Therefore, the EDTA-NaF method extracts both organic and inorganic P and may be suitable to extract available P in Thai soils high in iron and aluminum P and organic P.

The objectives of this research were 1) to estimate the P status in Thai soils, 2) to compare the amount of P extracted by EDTA-NaF and Bray II methods, and 3) to investigate the correlation between amount of high molecular weigh organic phosphate (HMWP) and different forms of organic P extracted by a modified Sekiya (1983) method.

Materials and methods

Soils. Topsoil (A horizon) and subsoil (B horizon) of 7 upland soils comprising Khorat series (Kt), Takhi series (Tk), Pakchong series (Pc), Banchong series (Bg), Nampong series (Ng), Lopburi series (Lb) and Satuk series (Suk) and 3 paddy soils comprising Rangsit series (Rs), Banglen series (Bl) and Chachoengsao series (Cc) were collected separately. The soil classification and land use of the collection sites are indicated in Table 1.

Plant debris was removed, and each soil sample was air-dried, passed through a 2-mm sieve and used for analysis of chemical properties of soils. Soil pH and electrical conductivity (EC) were measured in water (1:5, w/v). The amount of soil available P (Bray II-P) was extracted according to Bray and Kurtz (1945), and the concentration was determined by the molybdenum blue method (Murphy and Riley, 1962). The total P content was also determined by this method after digestion of the soils with $HClO_4$-HNO_3-HF in a teflon beaker. The total organic P was estimated from the 1 N H_2SO_4 extractable P in a soil sample ignited at 550ºC and an unignited sample (Olsen and Sommers, 1982) (ign P_o). The total organic carbon (OC) was determined using a modified Mebius procedure (Nelson and Sommers, 1982).

EDTA-NaF extract fractionation. Five grams of soil were weighed into a 250-ml bottle, add 100 ml of EDTA NaF (0.02 M EDTA-2Na +0.1 M NaF pH 5) added and the soil were shaken in a shaker (end-over-end) for 16 hours. The suspension was centrifuged, and the supernatant collected.

Table 1. Location, land use and soil classification of the soils.

Soil series name	**Location**	**Land use**	**Soil classification**
Khorat (Kt)	Phitsanulok	cassava	Oxic Paleustults; fine loamy, silicious
Takhi (Tk)	Nakhonsawan	cotton	Udorthentic Haplustolls; loamy skeleton carbonatic
Pakchong (Pc)	Kanchanaburi	cassava	Oxic Paleustults; clayey, kaolinitic
Banchong (Bg)	Chiengrai	maize	Oxic Paleustults; clayey, kaolinitic
Nampong (Ng)	Chiengrai	cassava	Ustoxic Quartzipsamments
Lopburi (Lb)	Lopburi	maize	Typic Pellusterts; very fine, montmorillonitic
Satuk (Suk)	Kamphaengphet	cassava	Oxic Paleustults; fine loamy, silicious
Rangsit (Rs)	Chachoengsao	paddy rice	Sulfic Tropaquepts; very fine, mixed
Banglen (Bl)	Nakhonpathom	paddy rice	Typic Haplaquolls; very fine, montmorillonitic
Chachoengsao (Cc)	Pathumthani	paddy rice	Typic Tropaquepts

A 15 ml of supernatant was digested with HNO_3-H_2SO_4 for the determination of total EDTA extractable P (EDTA ext P_t) by molybdenum blue method (Murphy and Riley, 1962). Another 15 ml of the supernatant was dialyzed against distilled water overnight, and the P content remaining in the dialyzed tube determined by the malachite green method (Motomizu *et al*, 1983) after it digestion with HNO_3-H_2SO_4. This P fraction represented HMWP. The amount of inorganic EDTA extractable P (EDTA ext P_i) in the soil was calculated by subtracting P in the HMWP from that in the EDTA ext P_t. The amount of non-EDTA extractable P (non-EDTA ext P) in the soil was calculated by subtracting P in the EDTA ext P_t from the total P.

Soil phosphorus fractionation. P forms in soils were fractionated using a modified Sekiya's method (Sekiya, 1983). Five hundred milligrams of soil was extracted with 30 ml of 2.5%(v/v) acetic acid and shaken using an end-over-end shaker for 2 hours. The soil suspension was centrifuged, and the supernatant was collected. The soil sample left in the tube was washed twice with 15 ml of 1 M NH_4Cl, and both washed solutions were added to the extract of acetic acid, which was then filled up to 60 ml with distilled water (solubilized Ca-P). After extraction of Ca-P form, the soil sample was extracted with 30 ml of 1 M NH_4F pH 7 and shaken using an end-over-end shaker for 1 hour and centrifuged, and the supernatant was collected (solubilized Al-P). The soil sample was then washed twice with 10 ml of saturated NaCl solution, which was discarded. The soil was subsequently extracted with 30 ml 0.1 M NaOH and shaken using an end-over-end shaker for 17 hours and centrifuged, and the supernatant was collected (solubilized Fe-P). Each extract was filtered through a 0.20 mm membrane filter. A fraction of each was digested with HNO_3-H_2SO_4 for the determination of the amount of total extracted P (ext P_t). The method of Murphy and Riley (1962) was used to measure the orthophosphate concentration in the neutralized extract [extracted inorganic P (ext P_i)] and in the neutralized digest of the extract (ext P_t). The amount of extracted organic P (ext P_o) in each extract was calculated by subtracting ext P_i from ext P_t.

Results

Soil chemical properties. Most of the soils, both topsoil and subsoil, were acidic (pH 4.04-6.28), except for Tk and Lb, which were moderately alkaline (pH 7.30-8.17) (Table 2). The electrical conductivity of all soil samples was low, except for the subsoil of Bl, which was slightly salty (2.50 dS m^{-1}). The total organic carbon varied greatly (0.03-4.12%) and mostly higher in topsoils than in subsoils. The total P concentration varied from 38 to1137 mg P_2O_5 kg^{-1}. The organic P varied from 17 to 579 mg P_2O_5 kg^{-1}, which contributed 33-67% of the total P. The available Bray II-P was

Table 2. Some chemical properties of the soils.

	Soil series	pH(1:5)	EC(1:5) (dS m^{-1})	% OC (%)	total P (mg P_2O_5 kg^{-1})	Bray II-P (mg P_2O_5 kg^{-1})	ignition P_o (mg P_2O_5 kg^{-1})
Upland soil	Kt_t[a]	5.56	0.02	0.40	303	11 (3.63)[c]	151 (49.83)[c]
	Kt_s[b]	5.47	0.01	0.19	235	7 (2.98)	96 (40.85)
	Tk_t	7.54	0.13	1.82	1137	38 (3.34)	579 (50.92)
	Tk_s	7.94	0.09	0.94	772	9 (1.17)	358 (46.37)
	Pc_t	6.45	0.21	4.12	827	28 (3.39)	498 (60.22)
	Pc_s	6.19	0.06	2.28	832	7 (0.84)	396 (47.60)
	Bg_t	5.76	0.04	0.94	737	34 (4.61)	279 (37.86)
	Bg_s	5.79	0.03	1.00	718	29 (4.04)	298 (41.50)
	Ng_t	6.07	0.06	0.41	115	6 (5.22)	69 (60.00)
	Ng_s	6.28	0.01	0.03	38	2 (5.26)	17 (44.74)
	Lb_t	7.32	0.09	1.88	538	76 (14.13)	254 (47.21)
	Lb_s	8.17	0.09	1.51	225	7 (3.11)	86 (38.22)
	Suk_t	5.44	0.05	0.47	248	6 (2.42)	138 (55.65)
	Suk_s	6.01	0.04	0.48	255	4 (1.57)	161 (63.14)
Paddy soil	Rs-t	4.16	0.32	2.38	553	1 (0.18)	372 (67.27)
	Rs_s	4.04	0.22	0.31	222	1 (0.45)	78 (35.14)
	Bl_t	6.74	0.58	1.17	415	22 (5.30)	169 (40.72)
	Bl_s	7.30	2.50	0.17	279	9 (3.23)	91 (32.62)
	Cc_t	5.72	0.41	1.04	360	22 (6.11)	173 (48.06)
	Cc_s	5.61	0.39	0.56	281	4 (1.42)	131 (46.62)

[a], top soil; [b], sub soil; [c], percentage in total P

very low to high (1-76 mg P_2O_5 kg^{-1}) and accounted for only 0.18-14.13% of the total P.

EDTA-NaF extract fractionation. In most soils, excluding alkaline soils, P extracted by EDTA-NaF reagent was obviously higher than that extracted by the Bray II reagent (Figure 1). The EDTA-NaF extracted P (HMWP+EDTA ext P_i) was 6-46% and 2-24% of total P in acid soils and alkaline soils respectively. This reagent extracted both high molecular weight phosphorus compound (HMWP) and inorganic fraction (EDTA ext P_i). The EDTA ext P_i tended to be larger than HMWP except in Tk soil (Table 3 and Figure 1). However, about 62-98% of total P could not be extracted (non-EDTA ext P).

Successive phosphorus extraction. The distribution of sum extractable organic and sum extractable inorganic phosphorus are shown in Table 3 and Figure 2. The amount of extracted inorganic P (sum ext P_i), calculated from the sum of Ca-P_i, Al-P_i and Fe-P_i, in soils varied from 9 to 368 mg P_2O_5 kg^{-1} (11-48% of the total P). Fe-P_i was the major fraction (4-42%) of extracted inorganic P, followed by Al-P_i (3-15%), whereas Ca-P_i accounted for only a small proportion (0-9%), except in topsoil of Tk and Lb, which were rich in Ca-P_i (12-18%).

The amount of extracted organic P (sum ext P_o) calculated from the sum of Ca-P_o, Al-P_o and Fe-P_o varied from 0-424 mg P_2O_5 kg^{-1} (0-57% of the total P). The amount of sum ext P_o in paddy soil (Rs, Bl and Cc) was low (0-11% of total P) compared with the upland soil (8-57% of total P). Most of ext P_o in all soil series was Fe-P_o, followed by Al-P_o. The amount of Ca-P_o was very low (0-2%), except in Tk (6-10%) (Figure 2).

Table 3 Amount of soil P extracted and non-extracted in different fractionation by EDTA-NaF extraction and by modified Sekiya method.

	Soil series	EDTA-NaF extraction			Modified Sekiya method									
		HMWP	EDTA ext Pi	non-EDTA ext P	ext Pi (mg P_2O_5 kg^{-1})				ext Po (mg P_2O_5 kg^{-1})				extractable P	residual P
		(mg P_2O_5 kg^{-1})	(mg P_2O_5 kg^{-1})	(mg P_2O_5 kg^{-1})	Ca-Pi	Al-Pi	Fe-Pi	sum ext Pi	Ca-Po	Al-Po	Fe-Po	sum ext Po	(mg P_2O_5 kg^{-1})	(mg P_2O_5 kg^{-1})
Upland soil	Kt_t^{a}	48 (16)^{c}	66 (22)^{c}	189 (62)^{C}	6 (2)^{c}	26 (9)^{C}	47 (16)^{C}	79 (27)^{C}	5 (2)^{C}	43 (14)^{C}	78 (26)^{C}	126 (42)^{C}	205 (69)^{C}	98 (31)^{C}
	Kt_s^{b}	8 (4)	40 (17)	186 (79)	3 (1)	22 (9)	41 (17)	66 (27)	0 (0)	8 (3)	41 (17)	49 (20)	115 (47)	120 (53)
	Tk_t	10 (1)	10 (1)	1117 (98)	203 (18)	115(10)	50 (4)	368 (32)	66 (6)	85 (7)	273 (24)	424 (37)	792 (69)	345 (31)
	Tk_s	4 (1)	5 (1)	763 (98)	78 (10)	96 (12)	59 (8)	233 (30)	78 (10)	53 (7)	202 (26)	332 (43)	566 (73)	206 (27)
	Pc_t	37 (4)	80 (10)	710 (86)	7 (1)	64 (8)	104 (13)	175 (22)	0 (0)	67 (8)	225 (27)	292 (35)	467 (57)	360 (43)
	Pc_s	26 (3)	21 (3)	785 (94)	0 (0)	20 (2)	91 (11)	111 (13)	0 (0)	48 (6)	166 (20)	214 (26)	325 (39)	507 (61)
	Bg_t	41 (6)	209 (28)	487 (66)	24 (3)	103 (14)	183 (25)	310 (42)	0 (0)	42 (6)	89 (12)	131 (18)	441 (60)	296 (40)
	Bg_s	37 (5)	183 (25)	498 (70)	22 (3)	94 (13)	199 (28)	315 (44)	0 (0)	42 (6)	107 (15)	149 (21)	464 (65)	254 (35)
	Ng_t	20 (17)	33 (29)	62 (54)	10 (9)	9 (8)	15 (13)	34 (30)	0 (0)	21 18)	45 (39)	66 (57)	100 (87)	15 (13)
	Ng_s	2 (5)	11 (29)	25 (66)	1 (3)	4 (11)	4 (11)	9 (25)	0 (0)	3 (8)	14 (37)	17 (45)	26 (70)	12 (30)
	Lb_t	18 (3)	115 (21)	404 (76)	64 (12)	37 (7)	60 (11)	161 (30)	0 (0)	15 (3)	112 (21)	127 (24)	288 (54)	250 (46)
	Lb_s	3 (1)	16 (7)	206 (92)	0 (0)	6 (3)	46 (20)	52 (23)	0 (0)	5 (2)	13 (6)	18 (8)	70 (31)	155 (69)
	Suk_t	28 (11)	49 (20)	171 (69)	6 (2)	23 (9)	34 (14)	63 (25)	0 (0)	30(12)	9 (4)	39 (16)	102 (41)	146 (59)
	Suk_s	30 (12)	56 (22)	169 (66)	4 (2)	20 (8)	37 (15)	61 (25)	0 (0)	41(16)	29 (11)	70 (27)	131 (52)	124 (48)
Paddy soil	Rs-t	52 (9)	53 (10)	448 (81)	1 (0)	31 (6)	235 (42)	267 (48)	0 (0)	25 (5)	35 (6)	60 (11)	327 (59)	226 (41)
	Rs_s	2 (1)	62 (28)	158 (71)	0 (0)	6 (3)	71 (32)	77 (35)	0 (0)	0 (0)	0 (0)	0 (0)	77 (35)	145 (65)
	Bl_t	2 (1)	21 (5)	392 (94)	3 (1)	12 (3)	61 (15)	76 (19)	0 (0)	4 (1)	9 (2)	13 (3)	89 (22)	326 (78)
	Bl_s	1 (0)	10 (4)	269 (96)	6 (2)	11 (4)	15 (5)	32 (11)	5 (2)	0 (0)	0 (0)	5 (2)	37 (13)	242 (87)
	Cc_t	22 (6)	93 (26)	246 (68)	12 (3)	53 (15)	79 (22)	144 (40)	0 (0)	8 (2)	27 (8)	35 (10)	179 (50)	181 (50)
	Cc_s	2 (1)	19 (7)	261 (92)	0 (0)	9 (3)	108 (38)	117 (41)	0 (0)	3 (1)	0 (0)	3 (1)	120 (42)	161 (58)

^{a}, top soil; ^{b}, sub soil; ^{c}, percentage in total P

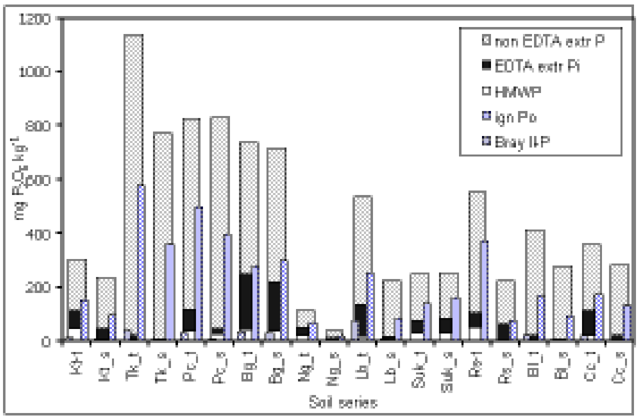

Figure 1. High molecular weight organic P (HMWP), inorganic P (EDTA ext P_i) and P which was not extracted (non EDTA ext P) by EDTA-NaF method compared with P determined by Bray II method (Bray II-P) and organic P determined by ignition method (ign P_o).

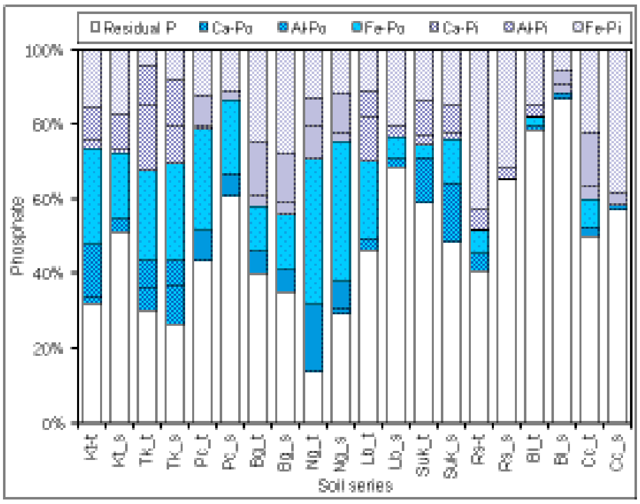

Figure 2. Phosphorus forms and percentage of each fraction in soil series.

Discussion

Phosphorus forms in Thai soils. The soil chemical properties of the 10 dominant soils series taken in Thailand varied greatly (Table 2) owing to the differences of soil texture and soil order. It was found that the soil reaction differed widely. Most of the soils were acidic, especially the Ultisols, due to the high weathering and leaching of basic cations during the soil development. These acid soils, containing high amounts of Fe and Al, are generally distributed in the tropical regions. However, the soil reaction of Tk and Lb soils was high (7.54 and 7.38 in the top soil, respectively) because their parent material was limestone; especially in Tk some weathering limestone was found. Therefore, the Ca-P_i in these soils is high compared with that in the acid soils. The major inorganic P fraction in acid soils was Al-P_i and Fe-P_I (Table 3). These results are consistent with the study of

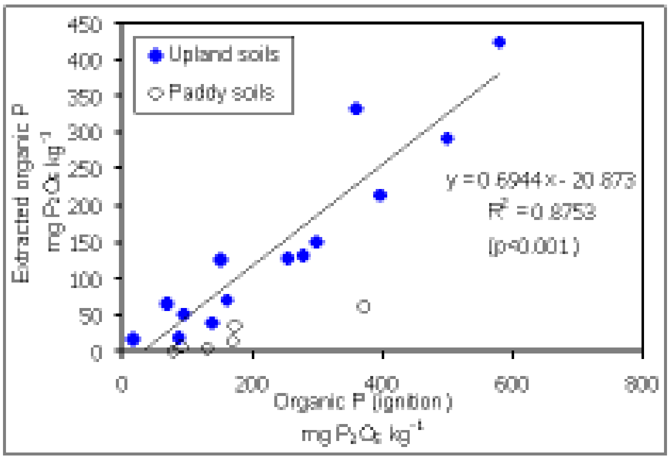

Figure 3. Relationship between extracted organic P and organic P (ignition) of upland soils and paddy soils.

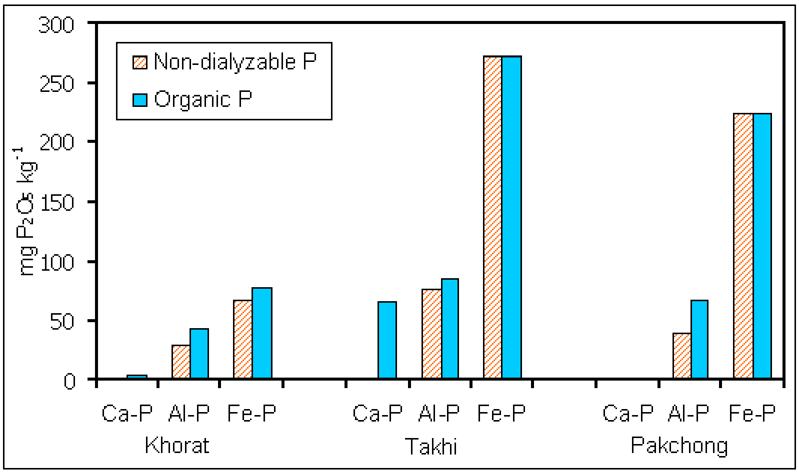

Figure 4. Comparison of P in acetic, ammonium fluoride and NaOH extract of Khorat, Takhi and Pakchong soil after dialyzing against water and organic P fraction calculated by subtracting inorganic P in extract from total P in each extract by modified Sikeya method.

P forms in highly weathered soils in peninsular Thailand (Onthong, 1999) and support the fact that inorganic P in tropical acid soils are mostly in the form of iron and aluminum phosphates (Stevenson, 1986; Foth and Ellis, 1997). The organic P fraction was also in the forms of Fe-P$_o$ and Al-P$_o$, except in Tk, which was high in Ca-P$_o$ (Table 3), indicating that the fraction of inorganic and organic P depends on the kinds of major cation (Ca, Fe and Al) in soil. The sum of Ca-P$_o$, Fe-P$_o$ and Al-P$_o$ highly correlated (R^2 = 0.8753) with organic P determined by ignition method (Figure 3). Therefore, by a combination of fractionation procedures of the modified Sekiya method (1983) and the digestion techniques, it was possible to fractionate organic P into Ca-P, Fe-P and Al-P as reported by Otani and Ae (1997). The non-dialyzable P (organic P remaining in the dialysis membrane) in each successive P extraction fraction from the modified Sekiya method was almost the same value of Ca-P_o, Fe-P_o and Al-P_o in Kt, Tk and Pc (Figure 4) thus strongly supporting the above conclusion.

Organic P in 10 dominant of Thai soils was 33-67% (Table 2), showing that it may be a large reserve of P for plants which are able to convert organic P in the rhizosphere to available P. The easily soluble fractions of soil organic P are often the most important factor in supplying P to plants in highly weathered soils. Generally, net P mineralization is most likely to occur if residues added to the soil have a C:P ratio lower than 200:1 (Brady and Weil, 1996). The C:P ratio of soil investigated varied from 40 to 189 (data not presented). Therefore, organic P in soil may be the main sources of P for plants grown in highly weathered soils. For this assumption, the reagent suitable for available P evaluation should be able to extract both inorganic and organic P that is available to plants.

P determined by the Bray II method and the EDTA-NaF method. The P extracted by Bray II reagent (0.03 M NH_4F+0.1 M HCl) was clearly lower than that of EDTA-NaF reagent (Figure 1) due to the fact that Bray II reagent extracted only inorganic P fraction loosely bound with Ca, Fe and Al, whereas the latter extracted fractions of both inorganic and organic P (Figure 1).

The Bray II method is widely used for evaluation of available P in both of upland and paddy soils in Thailand because of simplicity, rapidity and reliability (Saengthong and Cholitkul, 1989; Saengthong, 1991). This method extracts only some part of the Ca-P_i through dissolving calcium phosphates by HCl, Fe-P_i and Al-P_i through chelation with Fe and Al by fluoride ion (Kuo, 1996). This method performs unsatisfactorily in high calcareous soils due to the neutralization of the acid by calcium carbonate and formation of CaF_2, that reacts with dissolved P to form secondary precipitates (Kuo, 1996). However, the high amount of extracted P by Bray II-P in Tk and Lb, compared with the acid soils, is presumably due to the large amount of Ca-P in these soils that can be dissolved easily in the acidic extractant and the calcium carbonate content is not too high to limit the effect of the reagent. The Bray II method is suitable for determination of available P in acid soils (van Lagen, 1996) which comprises high amounts of Fe and Al phosphates, like most soils in Thailand (Saengthong and Cholitkul, 1989; Saengthong, 1991). The evaluation of available P in soils by Bray II method did not include the available P that plants perhaps derived from organic P, which was the main P fraction (Table 2).

The P extracted by the EDTA-NaF method was higher than that of Bray II method (Figure 1). This method can extract both organic and inorganic P (Figure 1), and the total amount of extracted P correlated well with Al-P_i and Fe-P_i (Figures 5a and 5b) which were the main fraction of inorganic P (Figure 2). It also correlated with HMWP (Figure 6), but HMWP did not correlate with organic P determined by the ignition method and Ca-P_o, Fe-P_o and Al-P_o, indicating that HMWP differs greatly among soils and does not depend on organic content in soils. This finding also implies that only HMWP may relate to available P in soils.

In the highly weathered soils, organic P is generally as high as 80% (Foth and Ellis, 1997), thus this fraction may supply P for plants. The suitable method for available P evaluation should extract some organic P in a similar was to that of plants. By secretion of some organic acids and phosphatase enzymes, it was reported that the organic fraction was possibly the P source for plants after it is converted to inorganic P by phosphatase enzymes, which were released from the plant roots or synthesized by soil microorganisms (Marscher, 1995). Moreover, the application of citric and oxalic acids to acid soils can extract organic P (Onthong *et al.*, 1999), therefore organic acids secreted by plant roots could possibly extract organic P.

The EDTA-NaF method is suitable in Japanese soils high in Al. From this current work, the EDTA-NaF method did not correlate well with the Bray II method ($R^2 = 0.2065$) (Figure 7), because of the EDTA-NaF method extracted both organic and inorganic P form while the Bray II method could not extract organic P form in the soil. However, recent work was confirmed that EDTA could

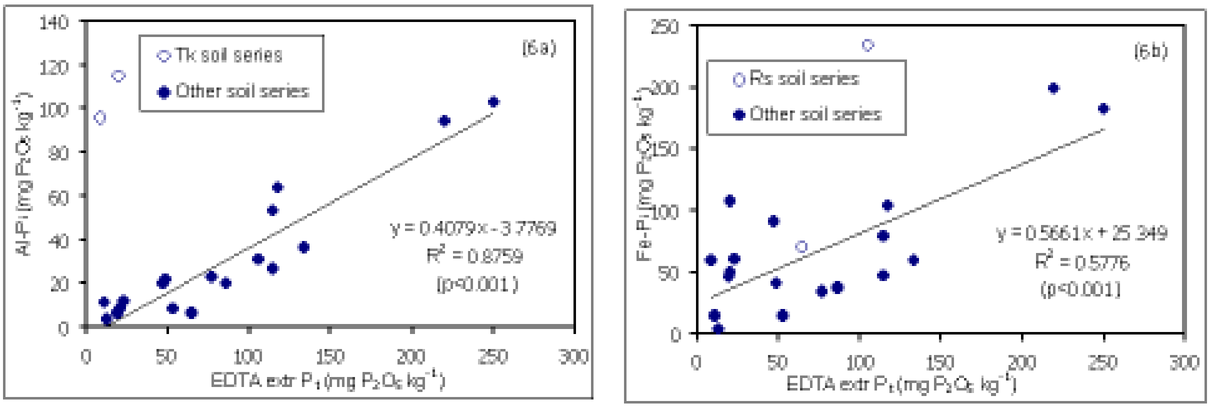

Figure 5. Relationship between total P extracted by EDTA-NaF method (EDTA ext P_t) and inorganic aluminum phosphates (Al-P_i) (5a) and inorganic iron phosphates (Fe-P_i) (5b) in Thai soils (not including Tk and Rs soil series).

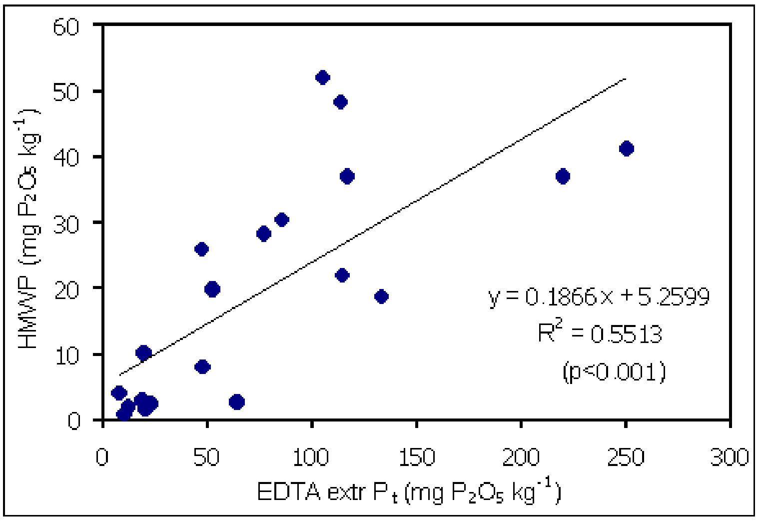

Figure 6. Relationship between high molecular weight organic P (HMWP) and total extracted P (EDTA ext P_t) by EDTA-NaF method.

enhance the utilization by plants of P in a hardly-soluble form and that fixed by soil (Pimsirikul *et al.*, submitted) due to the chelation with EDTA and possibly similar by due to organic acids secreted from the roots of the tropical plants. For this reason, a reagent containing EDTA may be a suitable method for P evaluation in soils which have high amounts of Fe-P_i, Al-P_i and organic P widely distributed in Thailand. However, the correlation between P extracted by this method and P uptake by plants must be tested, and the techniques should be developed to be simpler and more rapid for routine analysis.

Conclusion

The soil total P concentration in major soils in Thailand was 38-1137 mg P_2O_5 kg^{-1}. The avail-

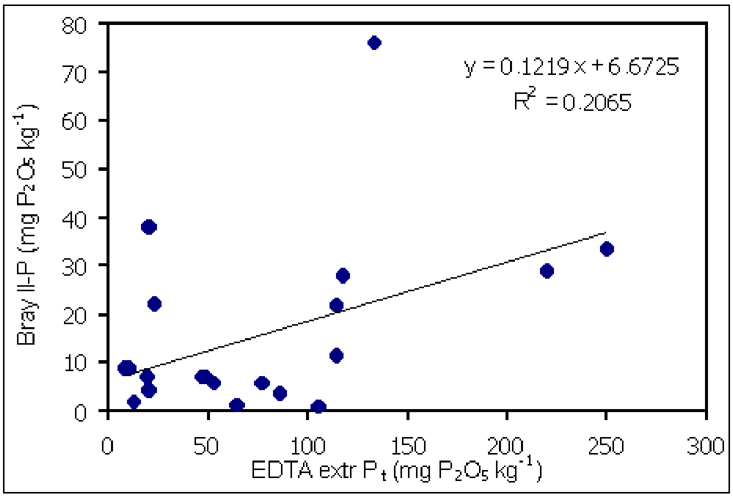

Figure 7. Relationship between P extracted by Bray II method (Bray II-P) and total P extracted by EDTA-NaF method (EDTA ext P_t).

able Bray II-P was very low to high (1-76 mg P_2O_5 kg^{-1}). Iron and aluminum phosphates were the main fraction of inorganic P in acid soil, whereas Ca phosphates were found in calcareous soils. Organic P content accounted for 33-67% and most of it was bound with Fe and Al in acid soils and Ca in calcareous soils. P extracted by EDTA-NaF reagent was obviously higher than that by Bray II reagent. The EDTA-NaF extracted P [high molecular weight organic P (HMWP) + inorganic P (EDTA ext P_i)] was 7-46% and 1-6% of total P in acid soils and calcareous soils respectively. The total amount of extracted P correlated well with Al-P_i and Fe-P_i, which were the main fraction of inorganic P. It also correlated with HMWP. The EDTA-NaF method may be suitable for P evaluation in soils which have high amounts of Fe-P_i, Al-P_i and organic P widely distributed in Thailand.

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